SELF-DIFFUSION PHENOMENA

IN THALLIUM AMALGAMS

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SELF-DIFFUSION PHENOMENA IN

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SUMMARY

Self-diffusion coefficients for 1.440 weight percent thallium amalgams were measured at 303°K, 323°K, 376°K, and 429°K and atmospheric pressure using the modified shear-cell technique developed by Broome and Walls. These values are in fair agreement with the values predicted by the Walls-Upthegrove Equation. The data were fitted to an Arrhenius type equation giving:

$$D = 5.58 \times 10^{-4} \exp(-1961.19/RT)$$

where D is in cm^2/sec.

CHAPTER I

INTRODUCTION

Over the past two hundred years an enormous amount of time and effort has been expended in attempting to understand the properties of the liquid state. The availability of experimental data is essential if proposed theories are to be evaluated. For a particular system, diffusion coefficients predicted by a number of theoretical models are often in better agreement than experimentally determined values. This fact emphasizes the definite need for further refinement of experimental methods.

The earliest study of diffusion in liquid metals was made by Homberg on mercury in 1739 (1). Since that time, numerous other attempts have been made using a variety of experimental techniques. These methods have been only moderately successful in providing data from which diffusion coefficients may be determined with accuracy. In fact, a precision of $\pm$10% is considered quite good for liquid metal systems. Greater precision is currently obtainable for aqueous or organic systems, where the surface tension effects are not as pronounced and where concentrations may be measured by optical methods.

A number of articles which review diffusion data and phenomena have been published (2,3,4); Edwards, Hucke, and Martin (4) have presented an exhaustive tabulation of self-diffusion and inter-diffusion coefficients which is a useful guide to the liquid metal systems for which data are published.

This study represents an attempt to improve the understanding of diffusion phenomena in liquid metals by using the modified shear-cell method to measure self-diffusion coefficients in an amalgam. The reliability of this method has been shown by Broome and Walls (5,6) and by Barras, Walls, and Hines (7). A thallium amalgam was selected because of its high solubility at the temperatures used in this work and because no published self-diffusion data for thallium amalgams at elevated temperatures exists.

CHAPTER II

DEFINITION AND SIGNIFICANCE OF DIFFUSION COEFFICIENTS

The knowledge of diffusion theory in liquid metals is poor as compared to solid or gaseous state diffusion phenomena. One of the main reasons for such poor understanding is that the knowledge of the liquid state itself is incomplete. This is further complicated by the lack of accurate diffusion data with which to test the various theories proposed to describe diffusion.

Adolph Fick (8) first proposed a diffusion model in which the flux of the diffusing species is proportional to the concentration gradient of that species. His model, known as Fick's first law, is expressed by the relationship:

$$J = -D \frac{\partial C}{\partial X} \tag{1}$$

where:

J = flux relative to the mass average velocity, mole/cm^2-sec

C = concentration of the diffusing species, mole/cm^3

X = position along the concentration gradient, cm

D = diffusion coefficient, cm^2/sec.

Combining the continuity equation and equation (1) gives Fick's second law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2} \tag{2}$$

where:

t = time of diffusion, sec.

A number of experimental techniques for measuring diffusion coefficients have been based on solutions of Fick's second law applied to various geometries. Several authors (9,10) have described such solutions for one dimensional binary diffusion by assuming that the diffusion coefficient is independent of concentration and that volume changes due to mixing are negligible.

Liquid metals literature usually discusses two types of diffusion: inter-diffusion, also known as chemical or mutual diffusion, and self-diffusion. Self-diffusion is the random motion of chemically indistinguishable atoms. In inter-diffusion, the motion of the atoms is random but the presence of a concentration gradient of chemically distinguishable atoms perturbs the motion of the atoms themselves and produces a net flux in the direction of decreasing concentration.

Experimental Methods

A number of experimental methods used for determining diffusion coefficients in liquid metals have been summarized by Walls (2) and by Edwards (4). Most of the methods involve the use of a radioactive tracer and some form of a confining capillary. The most popular of these are the capillary-reservoir, the long capillary, and the shear-cell method.

The capillary-reservoir technique, as described by Anderson and Saddington (11), is the most widely used, due to its experimental simplicity and its utility at high temperatures. In this method, a radioactive liquid is contained in an open ended capillary a few centimeters long and normally

about 1 mm in diameter. The capillary is immersed in a large bath of inert liquid and is slowly rotated. After a specified period of time, the capillary is removed from the bath and the composition of the metal in the capillary is compared with its initial composition. The main advantage of this method is that it allows several capillaries to be immersed simultaneously in the reservoir. One disadvantage of this method is the alteration of the initial concentration by surface tension effects when the capillary is immersed into the bath. Another disadvantage is the possible depletion of the tracer in the end of the capillary caused by its relative motion with the reservoir. Errors on the order of 10 percent must be expected due to these combined effects.

Carreri, Paoletti, and their co-workers (12,13,14,15,16) have described a long-capillary method, which employs a small diameter capillary tube about 150 to 200 mm in length. One half of the capillary is filled with material of one concentration and the other half is filled with a different concentration to complete the diffusion couple. Upon completion of the diffusion run, the capillary is cut into sections and the concentration profile is determined. Although the convection effects associated with the capillary-reservoir method are eliminated, melting, expansion, contraction, and solidification that occurs during a diffusion run, could cause serious error in the results.

The shear-cell technique consists of several discs mounted coaxially. Off center holes are drilled in each segment so that they may be aligned to form one long capillary. The metals of each composition are kept separate until the segments are aligned to form the diffusion path. After the diffusion run, the segments are separated and a concentration

profile is developed from the average concentration in each segment. A number of experimenters have used the various shear-cell methods to measure liquid metal diffusion coefficients. Of these, the four segment cell used by Nachtrieb and Petit (17) appears to have yielded the best data. Although many of the problems associated with the capillary-reservoir and long capillary methods have been eliminated, the filling problems and the mechanical complexities of the shear-cell method are formidable and have not been resolved despite a continued effort.

In considering the accepted diffusion techniques, several design criteria suggest themselves. Convection effects, such as those encountered with the capillary-reservoir technique, must be minimized. Second, the expansion and contraction problems of the long capillary and shear-cell methods need to be minimized. Third, the number of segments should be minimized to reduce mechanical complexity. In an attempt to solve these problems, Broome and Walls developed a modified shear-cell consisting of only two segments. Because of their success with this technique it was used in this work.

Review of Experimental Data

In Wilson's review of liquid metals (3), he states that pure component self-diffusion data are often subject to an error of $\pm$50% and self-diffusion coefficients of alloys may be in error by as much as 100%. Edwards, Hucke, and Martin (4) also reviewed liquid metal systems and found that some experimental data were quite reliable, while for others, an accuracy of $\pm$100% would be conservative.

A number of investigators (5,17,18,19,20,21,22) have reported

self-diffusion coefficients for pure mercury. The mercury diffusion data taken by Meyer (20) and by Broome (5) are probably representative of the best values and are in excellent agreement with each other over a wide temperature range. Meyer used the capillary-reservoir technique and measured self-diffusion coefficients in the temperature range from 273°K to 512°K, while Broome utilized the modified shear-cell method and reported diffusion coefficients from 248°K to 525°K.

Large concentration gradients of the bulk material, which cause convection effects, are absent in self-diffusion measurements. However, the diffusion coefficients have been found to vary with the capillary diameter, and with the material from which the capillary is made. This is especially true with self-diffusion coefficients in amalgams, since a slight density difference may occur in their preparation. Broome (23) studied the effect of a density difference on convection in a water-dye system and found that a density difference greater than .0001 gm/cc would result in convective flow. For the study of inter-diffusion, small effects like those discussed above are hidden by such gross effects as volume change occurring during the diffusion run and the presence of large concentration gradients.

Self-diffusion of one component in a binary alloy may be studied by bringing into contact two alloys of identical composition. One of these alloys contains radioactive tracers of the metal whose self-diffusion coefficient is to be studied, while the other alloy is prepared from inactive metals. Self-diffusion measurements in amalgams have been made by several investigators (21,24,25,26). Schadler and Grace (21) determined self-diffusion coefficients zinc amalgams

at several compositions, over the temperature range 273°K to 333°K, by the capillary-reservoir technique. They used their findings to verify Darken's (27) relationship between self-diffusion and inter-diffusion coefficients. Walls (24) also determined self-diffusion coefficients for zinc in zinc amalgams and cadmium in cadmium amalgams using the capillary-reservoir technique. Walls' zinc data, which was taken over the temperature range 323°K to 392°K at several compositions, is in good agreement with the data of Schadler and Grace. Walls' cadmium data shows considerable scatter and in some cases, exhibits an inverse temperature behavior. The self-diffusion coefficients for thallium amalgams were determined by Foley and Liu (25) for 8 compositions at 298°K, using the capillary-reservoir technique.

A large volume of data has been published for inter-diffusion in amalgams. Von Wogau (28) determined the inter-diffusion coefficients of lithium, sodium, potassium, rubidium, cesium, calcium, strontium, and barium in their respective amalgams at low temperature. Inter-diffusion coefficients for tin and bismuth in their respective amalgams were determined from polarographic data by Cooper and Purman (29). Mangelsdorf (30) studied cadmium amalgams at 298°K and 423°K by an electrolysis cell, using a thin ribbon shaped capillary. Von Meyer (31) used the shear-cell technique to determine the inter-diffusion coefficients of zinc, cadmium, and lead in amalgams at low temperatures. Stackelberg and Toome (32) used the dropping-amalgam electrode method to obtain the diffusion coefficients for cadmium, indium, lead, and sodium amalgams at 295°K. Cadium amalgams were also studied by Cohen and Bruins (33), using a polarographic method, and by Turner and Winkler (34) using the dropping-

amalgam electrode method. The polarographic method of measuring inter-diffusion coefficients was used by Furman and Cooper (35) for the study of zinc, cadmium, thallium, lead, and copper amalgams. Bonilla, Do-ik Lee, and Foley (36) determined the diffusivity of potassium-mercury systems by measuring their electrical resistivity. Edwards et al. (37) developed an experimental method of determining inter-diffusion coefficients with a concentration cell and reported inter-diffusion coefficients for potassium-mercury and sodium-tin systems, from 500°K to 900°K. Reid and Foley (38) measured the inter-diffusion coefficients for thallium in thallium amalgams using the capillary-reservoir method. The inter-diffusion coefficients for zinc and cadmium amalgams at low temperature were measured by Weischedel (39). Ravdel and Moshkevich (40) reported values of the inter-diffusion coefficients of lead and zinc in dilute amalgams from 273°K to 323°K, using the method of truncated capillaries.

The preceding survey has shown a definite lack of self-diffusion information on thallium amalgams in the literature. This research is an attempt to fill this gap.

Theoretical Model

Many theories have been conceived which attempt to predict the diffusion behavior of a liquid. Since these have been summarized in other works (2,4,), they will not be presented here. Only the Walls-Upthegrove equation, the relation used to correlate the data obtained in this paper, will be discussed.

The Walls-Upthegrove equation is based on Einstein's equation:

$$D = kTM \qquad (3)$$

which predicts the diffusion coefficient as a function of the mobility, M. M is defined to be the average velocity of the diffusing particle per unit force acting on that particle. The defining equation for the viscosity, which is used in evaluating M, may be written as:

$$F = A\ \mu \frac{dv}{dy} \tag{4}$$

where F is the force acting on the diffusing atom over an area A. In the general case the area may be expressed as:

$$A = \sigma d \tag{5}$$

where σ is defined as the area divided by the interatomic spacing, d. Since multiplying d by the velocity gradient in equation (4) gives the relative velocity, v_a, of an atom with respect to its neighbors, the mobility may be expressed as follows:

$$F = \mu\ \sigma d \frac{dv}{dy} = \mu\ \sigma\ v_A \tag{6}$$

Therefore:

$$M = \frac{v_A}{F} = \frac{1}{\sigma\mu} \tag{7}$$

To evaluate the mobility the arbitrary assumption is made that the forces acting on a diffusing atom are effective over the total surface area associated with the volume involved in the atoms movement as it diffuses over the length, d. This geometrical shape is a cylinder of length, d with hemispherical ends of radius r, thus:

$$A = 2\left[\frac{4\ \pi\ r^2}{2}\right] + 2\ \pi\ rd = 2\ \pi\ r(2r + d) \tag{8}$$

Solving for σ using equations (5) and (8):

$$\sigma = \frac{A}{d} = 2\ \pi\ r(2b + 1) \tag{9}$$

where b is the ratio of the atomic radius to the interatomic distance. Substituting equation (9) into equation (7) the mobility is found to be:

$$M = \frac{1}{2\ \pi\ r(2b + 1)\mu} \tag{10}$$

Thus:

$$D = \frac{kT}{2\ \pi\ r(2b + 1)\mu} \tag{11}$$

The theoretical analysis of diffusion behavior can be carried beyond equation (11) by introducing an expression for the liquid viscosity. Walls and Upthegrove chose Eyring's model (45) because it accurately predicts the viscosity for a large number of liquids. Eyring's equation is:

$$\mu = \frac{N_o\ h}{V} \exp -\frac{\Delta S^*}{R} \exp \frac{\Delta H^*}{RT} \tag{12}$$

Substituting equation (12) into equation (11) gives:

$$D = \frac{kTV}{2\ \pi\ r(2b + 1)N_o\ h} \exp \frac{\Delta S^*}{R} \exp -\frac{\Delta H^*}{RT} \tag{13}$$

The atomic radius, r, used in equation (13) is extremely difficult to determine. It is possible to eliminate r by introducing the expression:

$$V = a_3\ \sigma^3$$

or:

$$\sigma = \left[\frac{V}{a_3}\right]^{1/3} = 2\ \pi\ r(2b + 1) \tag{14}$$

where a_3 is a proportionality constant. Substituting equation (14) into equation (13) gives:

$$D = \frac{kT\ (a_3)^{1/3}\ V^{2/3}}{N_o\ h}\ \exp\frac{\Delta S^*}{R}\ \exp -\frac{\Delta H^*}{RT} \qquad (15)$$

The last problem is to evaluate a_3 only in terms of the parameter b. This is done by using a configuration constant relating the molar volume to the interatomic spacing, and by using the relation between σ and r as given in equation (14). The configuration constant is dependent only on the geometry of the liquid structure and is defined as:

$$\gamma = \frac{N_o\ d^3}{V} \qquad (16)$$

γ is determined by the largest number of nearest neighbors surrounding an atom. For liquids with a coordination number of eight to eleven a reasonable choice for γ is 4/3. Combining equations (16) and (14) and solving for a_3 gives:

$$a_3 = \frac{N_o}{\gamma[2\ \pi\ b(2b + 1)]^3} \qquad (17)$$

Substituting equation (17) into equation (15) gives the Walls-Upthegrove equation:

$$D \approx \frac{kT\ \gamma^{-1/3}}{2\ \pi\ h\ b(2b + 1)}\left[\frac{V}{N_o}\right]^{2/3}\ \exp\frac{\Delta S^*}{R}\ \exp -\frac{\Delta H^*}{RT} \qquad (18)$$

where:

D = the self-diffusion coefficient, cm^2/sec

k = Boltzman's constant, erg/°K

T = temperature, °K

γ = configuration parameter dependent on the coordination number of the liquid

h = Planck's constant, erg/sec

b = geometrical parameter defined as the ratio of the diffusion particle radius to the interatomic spacing

V = molar volume, cm^3/gm-mole

N_o = Avogadro's number, $(gm\text{-}mole)^{-1}$

ΔS^* = entropy of activation for kinematic viscosity, cal/gm-mole°K

ΔH^* = enthalpy of activation for kinematic viscosity, cal/gm mole.

The enthalpy and entropy of activation can be determined from kinematic viscosity data, and the third parameter, b, has been given by Walls (24) as .419.

The Walls-Upthegrove equation was developed for pure liquid metal systems. Walls and Upthegrove compared the values predicted by their equation to available self-diffusion data on sodium, mercury, cadmium, tin, gallium, zinc, lead, indium, copper, and silver. They concluded that their model fit the available self-diffusion data more accurately than other diffusion models.

The extension of the Walls-Upthegrove equation to binary systems is simply a matter of changing the molecular weight of the pure component to the average molecular weight of the amalgam, and using binary density and viscosity data to evaluate ΔS^* and ΔH^*. The use of the equation with binary systems is shown in Appendix D.

CHAPTER III

INSTRUMENTATION AND EQUIPMENT

Diffusion Cells

The modified shear-cell as described by Broome and Walls (5) was used in this work. It is a combination of other shear-cell methods and the long capillary design in which the better features of both techniques have been incorporated, and many of the problems which caused mathematical and experimental difficulties have been eliminated.

The modified shear-cell, shown in Figure 1, consists of two elements; one segment is fixed to a baseplate, while the second slides along a slot cut into the baseplate. It is the relative motion between the two segments which allows them to form or shear the diffusion capillary. The fixed segment is filled with inert amalgam, while the moving segment contains a radioactive amalgam of the same composition.

The diffusion coefficient can be determined from measurements of the net exchange of radioisotope between the two segments of the capillary column.

Three sets of matched cells were used in this work. The capillary diameters were approximately 1.2, 1.5, and 1.6 millimeters and all were approximately 30 millimeters long. The stopcock at the rear of the capillary was used for filling the capillary. It had a large diameter in comparison with the capillary diameter, so that when in the closed position it would provide an essentially flat end to the capillary.

Overlow tubes were provided so that a capillary extended into the

other segment. These tubes were located so that the capillary and its overflow could be simultaneously aligned. This allowed expansion to take place in the overflow tubes prior to connecting the capillaries in each side. Consequently the expansion problem encountered in the long capillary method is avoided. Once the entire system had equilibrated at the diffusion temperature, the cells were sheared and the two capillary segments came into contact to form the diffusion couple. After the capillary and its overflow were sheared the overflow was isolated and never came into contact with the diffusion amalgams.

The overflow tubes aided in initially filling the capillaries and helped to equalize the pressure between the two sections of the capillary segments at the diffusion temperature. Without the overflow tubes, the high surface tension of the amalgam would make complete filling of the capillary extremely difficult. Incomplete filling could result in the necking of the liquid thread at the shear interface and give erroneous diffusion coefficients.

The cell segments were aligned by a motor driven pushrod which pushed the movable segment across the baseplate. A mechanical stop was placed on the baseplate so that the drive motor was stalled when the movable segment slid into the proper horizontal alignment. Spring loaded screws were used to fasten the movable segment onto the baseplate to give vertical alignment of the capillaries. A spring loaded bar at the rear of the movable segment assured sealing at the interface. Any materials to be used in the fabrication of the cells must: 1) be compatible with the amalgam in the temperature range of the study, 2) be machinable to a very high degree of precision, and 3) take a very

smooth finish. For this work the cell segments, baseplate, and drive assembly were made of low carbon steel. The stopcocks were made of hardened drill rod to preserve the finishes in the hole and on the stopcock.

Ovens

The diffusion runs were carried out in two specially constructed laboratory ovens. One oven was constructed of 1" Marinite and was controlled by a Fisher proportional temperature controller. Heat was supplied to the oven by two 675 watt flat heating elements wired in parallel. The other oven was constructed from Transite and firebrick. A schematic of its heating elements is shown in Figure (2). The ballast heat to this oven was supplied by a Powerstat variable transformer type 3PN1178 connected to the ballast heater circuit. The voltage was adjusted on the Powerstat until the oven temperature was about 20°K lower than the desired diffusion temperature. The remaining heat was supplied by a second heater controlled by a R7355C 3 mode controller coupled with a Honeywell R7291A SCR Power Module. The temperature in the Marinite oven was maintained at $\pm$.5°K and the temperature in the Transite oven was maintained within $\pm$1°K. The temperatures were measured with calibrated iron-constantan thermocouples using a Leeds and Northrop 8686 millivolt potentiometer. A Honeywell Electronik 193 strip chart recorder was used to monitor the temperature deviation during the runs. The Marinite oven was used for the majority of the runs because it had less insulation which allowed it to dissapate heat faster and therefore give better control in the temperature range of the study.

A Precision Scientific model 524 vacuum oven was used to degas the amalgams in the diffusion cells before placing them in the diffusion ovens. The vacuum oven was operated at 403°K and 380 mm of mercury for 8 hours for the runs made at 323°K, and at 403°K and 78 mm of mercury for the rest of the runs.

Stock Materials

The thallium used in the diffusion measurements was obtained from ICN Parmaceuticals - K&K Laboratories Inc. with a purity of 99.999%. The thallium radioisotopes were produced in the Georgia Tech research reactor at the Frank H. Neely Nuclear Research Center. The thallium rods were .48 cm in diameter and approximately 5 cm long. They were radiated in a flux of 8×10^{12} Neutron (Thermal)/cm^2-sec for 8 hours. The mercury used was reagent grade Caulk 20th Century Mercury, 99.9% pure.

Power Packs

The voltage source used to hold the amalgams in solution in this experiment was an Electronic Measurements Co. Model TR018-1, which maintained a potential across the electrodes of 12 volts and drew a current of less than .5 milliamperes.

Counting Equipment

Two reliable methods of counting beta radiation were available, a liquid scintillation counter and a gas flow proportional counter. The Nuclear-Chicago Mark I Liquid Scintillation Counter was chosen because of the ease of sample preparation and because it is a more efficient beta counter with an efficiency of 25.75%. The amalgam samples to be counted

were collected and dissolved in 20 ml liquid scintillation vials. This was accomplished by pipetting 20 ml of a 50 volume % nitric acid solution into each vial and allowing it to stand for two hours.

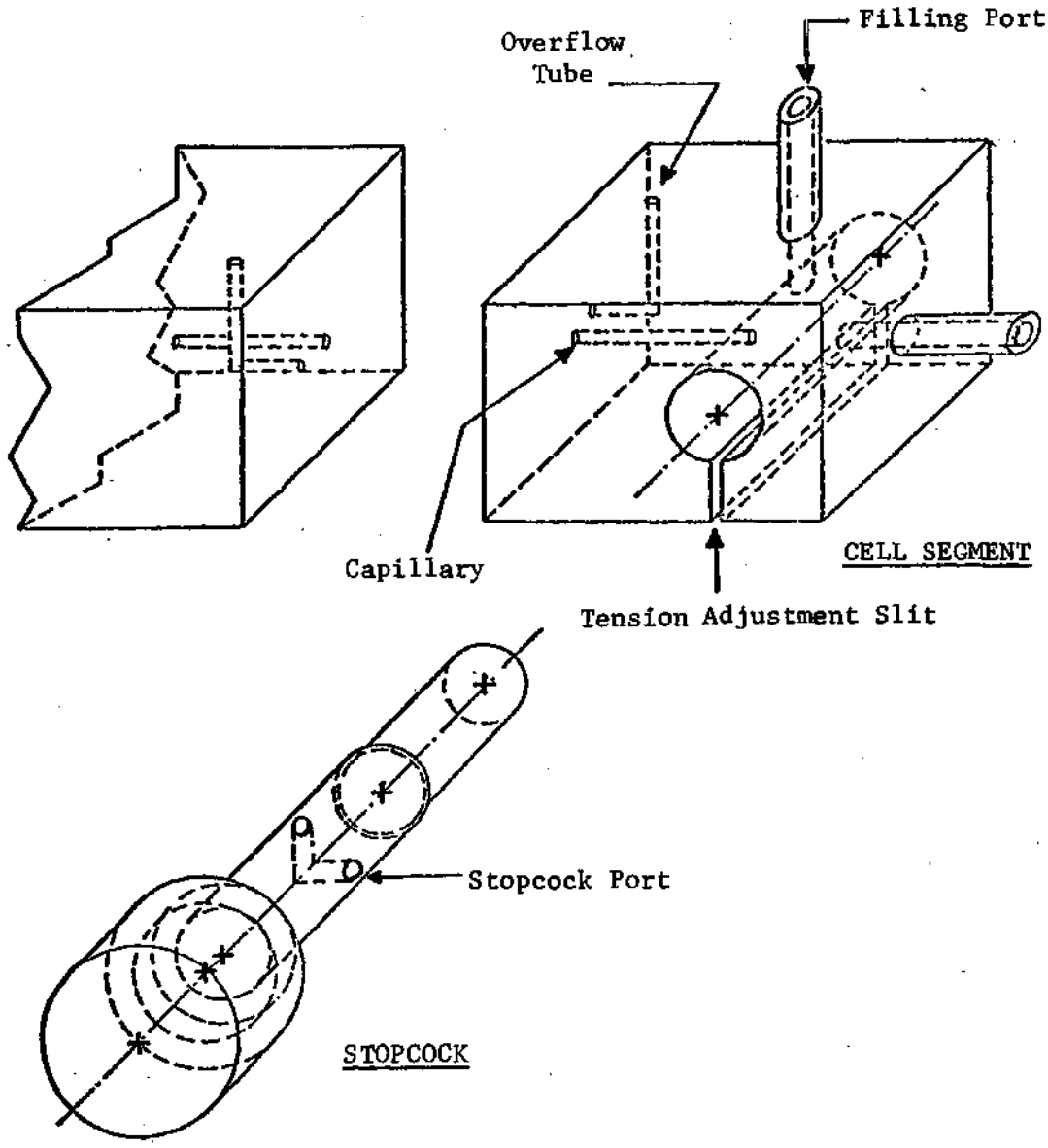

Figure 1. Schematic of Cell Segment

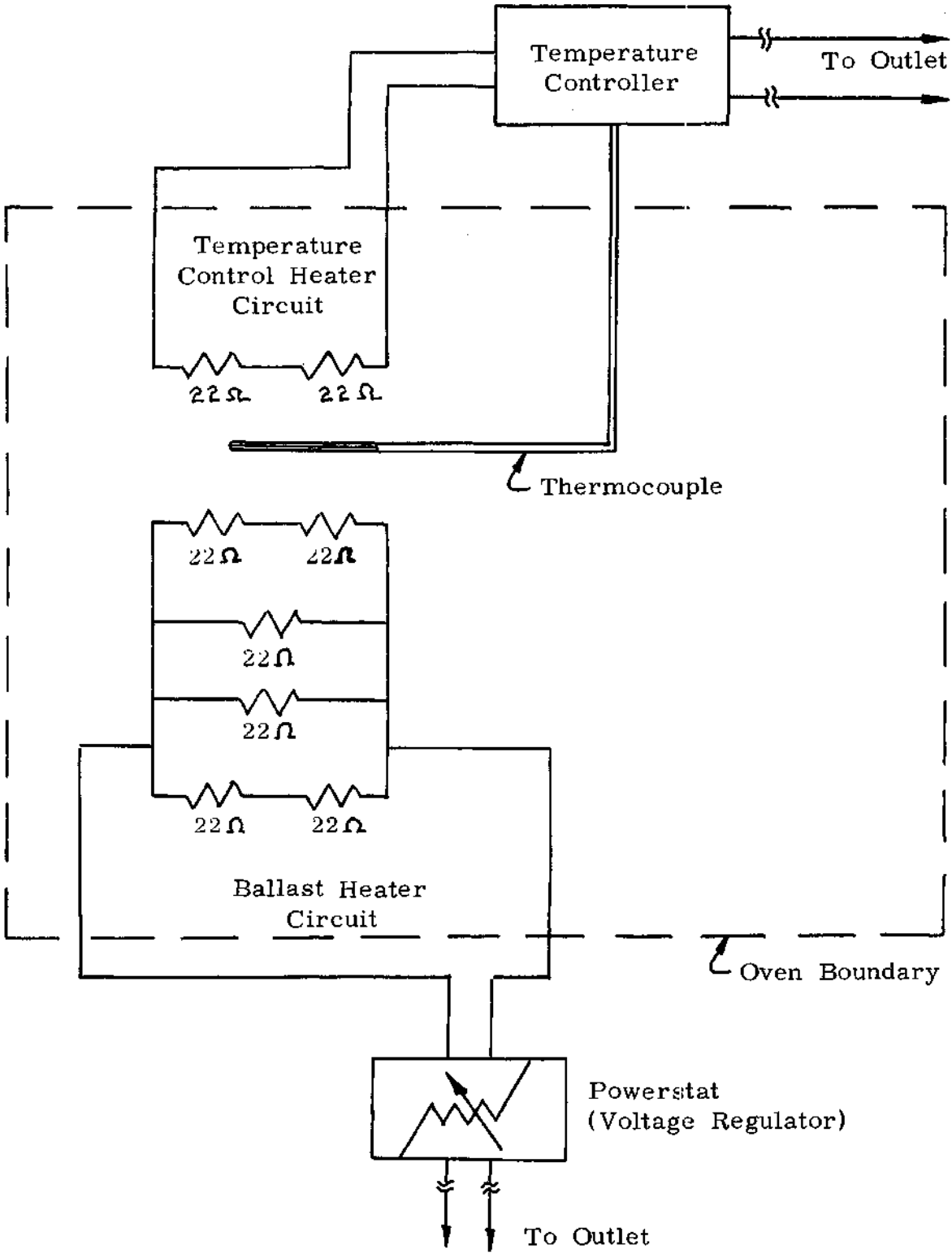

Figure 2. Schematic of the Heating Elements in the Transite Oven

CHAPTER IV

PROCEDURE

The thallium amalgams used in this work were prepared by weighing an amount of mercury and then adding the weight of solid thallium needed to make the desired 1.440 weight % composition. The thallium was first prepared by washing it in concentrated nitric acid for a few seconds to dissolve the oxide layer. The metal was then rinsed in distilled water and carefully dried with Kimwipes. To prevent weight change due to the rapid oxidation of the thallium it was cut and filed as quickly as possible until it was within +.0001 gram of the desired weight. The thallium was then placed in a glass cell containing the mercury and a layer of distilled water was placed over the amalgam. To prevent preferential oxidation of the thallium the technique of Crenshaw (42) was utilized, in which a 12 volt potential was placed across the cell using a platinum wire in the distilled water as the anode and the thallium amalgam as the cathode.

Prior to a diffusion run, the shear cells were cleaned, dried and lubricated. Periodic checks for radioactive contamination revealed there was no detectable contamination in the empty diffusion cells. The alignment of the capillary in the assembled shear-cell apparatus was carefully checked before filling the cells with the amalgams. This was done by making certain that no discontinuity could be felt on the sides of the cell segments as they rested against the mechanical stop in the aligned position. The movable segment of the cell was then adjusted

until the capillaries were aligned with their respective overflow tubes. The matching faces of the cells were checked for misalignment by making sure that no light could be seen between the faces. The amalgams were then loaded into the cell with a dropping pipet. The cells were placed in the vacuum oven for 8 hours to outgas the amalgams. After the shear cell assembly was removed from the oven, it was allowed to cool for about 1 hour. The stopcocks were then rotated and the excess amalgam in the filling ports was removed. Approximately .6 gram of amalgam was used for the diffusion measurement in each cell segment. The assembled diffusion cells were placed in the diffusion oven and the cell baseplate was leveled so that the capillaries were horizontal. The temperature controller and the ballast heaters were then turned on. When the cell assembly had reached the desired temperature, the diffusion measurement was begun by driving the movable segment against the mechanical stop to form the capillary diffusion couple. After a measured time interval, usually 8-10 hours of isothermal diffusion, the stop was removed, and the capillary column was sheared by driving the movable segment aside until the capillary segments were isolated from each other. The diffusion cell was allowed to cool and was removed from the oven.

The diffusion cell was then disassembled and the capillaries were emptied into the liquid scintillation vials. This was done by placing the pipet bulb over the overflow port and squeezing to remove excess amalgam left in the overflow tubes, and then placing the pipet bulb over the filling ports and squeezing the bulb to force the capillary contents into the vials. The weight of the amalgam in each vial was measured to determine if portions of the amalgam had been lost

in the handling procedures. The samples were then dissolved by pipetting 20 ml of 50 volume % nitric acid into the vials. The radioactivity of each sample was determined by the liquid scintillation counter. Initial hotside count rates of 5,000 - 40,000 cpm were obtained. The final hotside count rates ranged between 4,000 - 42,000 cpm while the final coldside count rates ranged between 1,000 - 15,000 cpm. The samples were counted for at least 1,000,000 counts to reduce error in the count rates. Counting usually took from 1/2 to 16 hours for each sample, depending on the count rate.

CHAPTER V

RESULTS AND DISCUSSION

The self-diffusion coefficients for 1.440 weight % thallium amalgams were measured by the modified shear-cell technique designed by Broome and Walls. The measurements were made at atmospheric pressure over the temperature range, 303°K to 429°K, and are presented in Table 1. Equation (B-17), which is the solution to Fick's second law for the finite capillary geometry of the modified shear-cell, was used in the computer program given in Appendix C to calculate the self-diffusion coefficients.

To compare these results with other works, the self-diffusion coefficients were fitted to the Arrhenius type equation giving:

$$D = (5.58 \times 10^{-4}) \exp\left(\frac{1961.19}{RT}\right) \qquad (19)$$

where:

D = self-diffusion coefficient, cm^2/sec

R = gas constant, (1.98717), cal/(mole-°K)

T = temperature, °K.

The values of the activation energy and the pre-exponential factor in this work are compared to values from other works in Table 2. The values for the pre-exponential factor for the thallium amalgam were more than twice Barras' value for pure thallium and five to six times the pre-

Table 1. Measured Self-Diffusion Coefficients in Thallium Amalgams at 1.440 Weight Percent Thallium

Temp °K	D x 10^5 (cm^2/sec)	Time (sec)	Beta	±Δ Beta	±Δ D x 10^5 (cm^2/sec)
305.7	1.4895	36469.	.7230	.0024	.03
303.2	1.2056	36803.	.7428	.0025	.03
303.2	2.3388	32396.	.6731	.0024	.03
303.2	1.5564	41999.	.6892	.0024	.02
303.2	1.7196	31747.	.7163	.0024	.03
303.2	1.0959	29898.	.7844	.0025	.03
303.2	2.3846	26047.	.6984	.0024	.04
322.7	1.9693	33780.	.6935	.0121	.15
322.7	2.8087	30840.	.6424	.0117	.19
322.7	2.1066	27300.	.7083	.0122	.18
322.7	4.4044	28380.	.5709	.0112	.23
322.7	3.7564	29580.	.5953	.0113	.21
322.7	1.3060	26705.	.7724	.0126	.15
322.7	3.9242	32531.	.5759	.0112	.21
322.7	3.3760	28380.	.6324	.0116	.22
322.7	3.0299	24826.	.6667	.0024	.03
322.7	2.8000	31565.	.6469	.0023	.04
322.7	1.4519	33538.	.7315	.0025	.03
322.7	3.5324	35944.	.5752	.0022	.04
322.7	3.2052	37085.	.5884	.0023	.04
322.7	2.7543	31429.	.6466	.0024	.04
322.7	3.3718	30972.	.6163	.0023	.04

Table 1.(Continued)

Temp °K	D x 10^5 (cm^2/sec)	Time (sec)	Beta	±Δ Beta	±Δ D x 10^5 (cm^2/sec)
322.7	3.7666	32445.	.5829	.0023	.04
375.7	3.1761	27743.	.6394	.0023	.04
375.7	4.1149	31926.	.5698	.0022	.04
375.7	2.6137	48794.	.5665	.0022	.03
375.7	4.6185	24489.	.6007	.0023	.05
375.7	2.8593	25502.	.6718	.0024	.04
375.7	3.3040	34804.	.5883	.0022	.04
375.7	2.7918	31500.	.6478	.0023	.04
375.7	4.0879	25234.	.6186	.0023	.05
375.7	2.9534	32100.	.6260	.0023	.04
375.7	4.5415	33839.	.5349	.0022	.04
375.7	4.9379	30000.	.5331	.0022	.05
375.7	6.3087	33454.	.4445	.0020	.04
375.7	3.8544	30016.	.5938	.0023	.04
375.7	2.7792	33175.	.6358	.0023	.04
375.7	5.6074	33303.	.4879	.0021	.05
378.7	3.0822	28044.	.6469	.0024	.04
375.7	2.8719	25292.	.6798	.0024	.04
419.2	5.2485	34978.	.4810	.0021	.04
429.2	6.9154	34978.	.4193	.0020	.05
429.2	4.5664	32756.	.5402	.0022	.05
429.2	6.7695	25800.	.5064	.0022	.06
429.2	6.4530	27794.	.4869	.0021	.05

Table 1. (Continued)

Temp °K	D x 10^5 (cm^2/sec)	Time (sec)	Beta	+Δ Beta	+Δ D x 10^5 (cm^2/sec)
429.2	5.6793	28886.	.5193	.0022	.05
429.2	4.6758	29727.	.5562	.0022	.05
399.2	6.1456	28886.	.4895	.0021	.05
429.2	4.6313	42515.	.4753	.0021	.04

Table 2. Experimental Self-Diffusion Constants for the Arrhenius Equation for Liquid Metal Systems

System	Concentration	Do (cm^2/sec)	E (cal/mole)	Temperature Range (°K)	Reference
Hg-Tl	1.414 At % Tl	5.58×10^{-4}	1961.2	303-429	This Work
Tl	Elemental	2.21×10^{-4}	2867	590-724	7
Hg	Elemental	1.26×10^{-4}	1160	-	2
Hg	Elemental	1.10×10^{-4}	1150	296-333	18
Hg	Elemental	$.85 \times 10^{-4}$	1005	273-371	17

exponential factor for pure mercury. The activation energy for the thallium amalgam fell approximately half-way between Barras' value for pure thallium and the values for pure mercury. In Figure 3 the experimental data of this work is compared to the self-diffusion coefficients predicted from the Walls-Upthegrove equation. The required density and viscosity data for the thallium amalgams were obtained from a paper by Foley, Basak, and Delorey (44). The parameters b and Y were presented by Walls (24). The entropy of activation, $\Delta S^* = -1.54$ cal/mole °K, and the enthalpy of activation, $\Delta H^* = 610.92$ cal/mole, were determined by curve fitting the kinematic viscosity data obtained from Foley, Basak, and Delorey to the following equations taken from Eyring's viscosity equation:

$$\nu = B \exp\left(\frac{\Delta H^*}{RT}\right) \tag{20}$$

and:

$$B = \frac{N_o\, h \exp\left(\frac{-\Delta S^*}{R}\right)}{N_1 M_1 + N_2 M_2} \tag{21}$$

where:

ν = kinematic viscosity, cm^2/sec

N_o = Avogadro's number, (6.02×10^{23}) molecules/mole

h = Planck's constant, (1.38×10^{-16}) erg/°K

N_1, N_2 = atomic fraction of component 1 or 2

M_1, M_2 = molecular weight of component 1 or 2

ΔH^* = enthalpy of activation, cal/mole

ΔS^* = entropy of activation, cal/(mole-°K)

R = ideal gas constant (1.98717), cal/mole-°K

T = temperature °K.

Sample calculations using the Walls-Upthegrove equation are given in Appendix D.

Foley and Liu have reported self-diffusion data for thallium amalgams (2,5). They report data at 298°K for compositions of .75, 7.13, 16.10, 20.04, 28.56, 34.60, 38.68, and 41.58 atomic percent thallium. Interpolation of their results to 1.414 atomic percent (1.440 weight percent) thallium, yields a diffusion coefficient of $.98 \times 10^{-5} cm^2/sec$. Extrapolation of the data presented in this work to 298°K yields a value of $2.05 \times 10^{-5} cm^2/sec$. This indicates that the data from this work are approximately 100% higher than the value obtained from Foley and Liu. Foley and Liu used the capillary-reservoir technique, with a capillary diameter of 1 mm, while the capillary diameters used in this work were approximately 1.5 mm in diameter. Edwards, et al., (4) concluded that even under favorable conditions, convection effects will be appreciable for experiments conducted with capillary diameters of greater than a few mm. However, wall effects could be more pronounced with the smaller diameter capillaries and thus have strong influence on the diffusion coefficient. The optimum capillary diameter however was not investigated in this work.

The major problem encountered in this research was the formation of gas bubbles in the capillaries. This prevented the capillaries from being completely full and caused the diffusion thread to be broken in one side of the capillary. Any runs in which the capillaries were not completely filled were discarded. Vacuum degassing at elevated temperatures for several hours was tried in an attempt to alleviate this problem. Use of this method showed a good deal of improvement in the results.

However, it met with only limited success for runs made at 429°K, as indicated from the data scatter at this temperature.

Another problem encountered was slight variations in the count rate which, according to equation (B-18), produced large variations in the diffusion coefficient. This problem was lessened by taking large numbers of counts, usually 1 million, to reduce the random counting error. The errors in the self-diffusion coefficients, resulting from counting error are shown in Table 1.

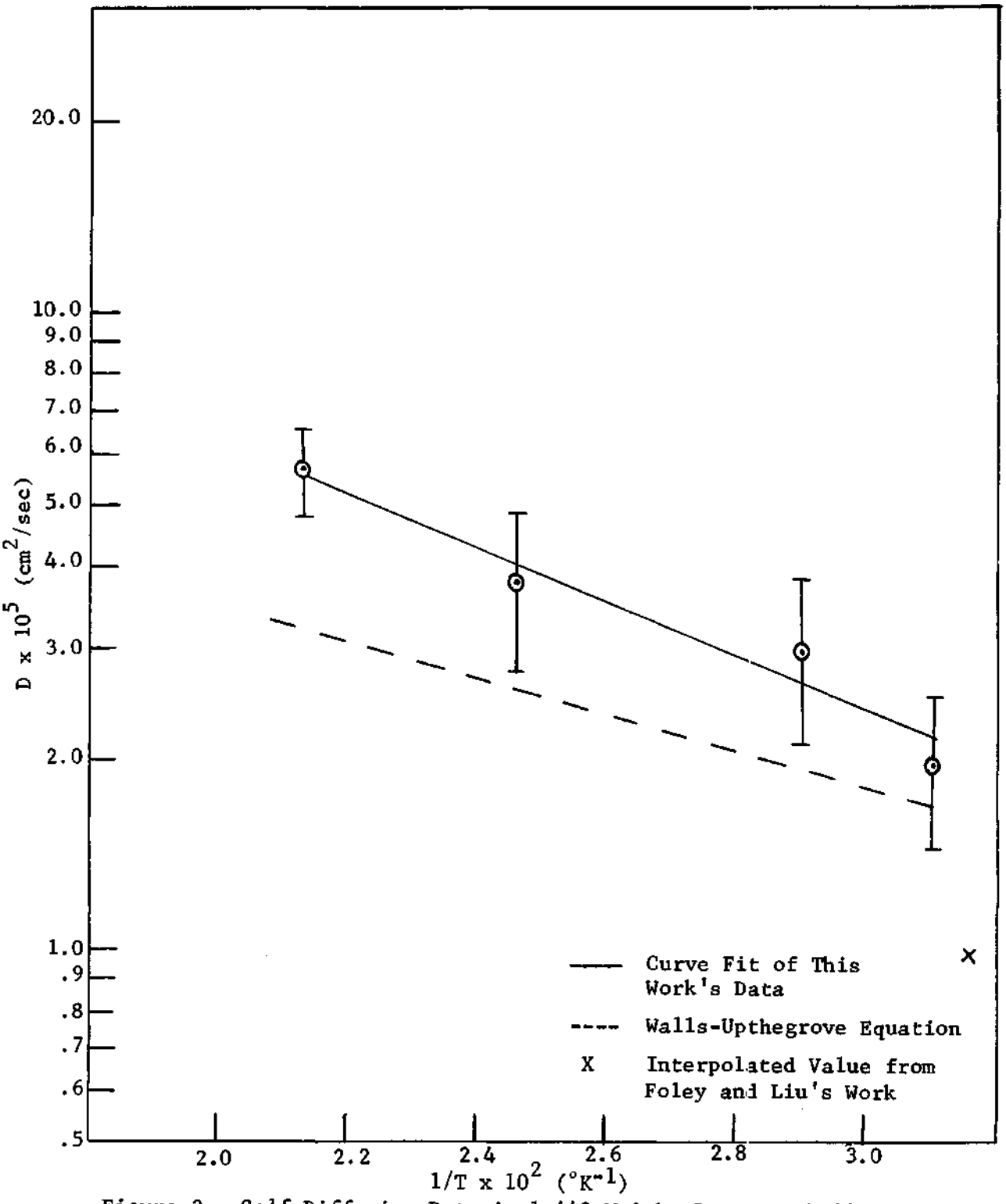

Figure 3. Self-Diffusion Data in 1.440 Weight Percent Thallium Amalgams

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The measurements of self-diffusion coefficients in 1.440 weight % thallium amalgams were successfully made in the temperature range from 303°K to 429°K at atmospheric pressure by the modified shear-cell technique developed by Broome and Walls. The self-diffusion coefficients are in fairly good agreement with the values predicted by the Walls-Upthegrove equation using the experimental viscosity and density data of Foley, Basak, and Delorey (44).

It is recommended that a vacuum degassing system with a vacuum greater than 78 mm of mercury and a temperature capability greater than 323°K be utilized in the preparation of diffusion samples prior to making a diffusion run. It is also recommended that a better counting method be used to determine the radioactive count rate. The liquid scintillation counter is extremely sensitive to the vial thickness, the amount of liquid used to dissolve the samples, and slight variations in color.

This work and other works on self-diffusion in liquid metals have shown that a better understanding of the effect of the capillary diameter on the self-diffusion coefficient is needed to minimize experimental error. It is recommended that a study of the effect of the capillary diameter on the diffusion coefficient be made for the modified shear-cell technique.

APPENDIX A

NOMENCLATURE

A_o, A_n	-	constants arising from solution to Fick's second law
b	-	a geometrical parameter which is defined as the ratio of the diffusing particle radius to the interatomic spacing
B	-	constant in the kinematic viscosity equation, cm^2/sec
D	-	diffusion coefficient cm^2/sec
D_o	-	pre-exponential factor in Arrhenius equation, cm^2/sec
cpm	-	concentration in radioactive counts per minute
C	-	concentration
C_i	-	quantity of radioactive material disintegrating at the rate of 3.7×10^{10} atoms/sec
C_{avg}	-	average of C_s and C_o at $t = \infty$, cpm
C_f	-	final capillary concentration in the capillary-reservoir technique, cpm
C_o	-	initial concentration in the capillary in the capillary-reservoir technique and in the radioactive side of the shear-cell technique, cpm
C_r	-	reservoir concentration in capillary-reservoir technique, cpm
C_s	-	non-radioactive capillary concentration in the shear-cell technique, cpm
$C_2(t)$	-	average concentration of the radioactive capillary at time, t, in the shear-cell technique, cpm
E	-	activation energy for the Arrhenius equation, cal/gm-mole
H_i	-	error in iterative solution to the shear-cell diffusion equation
ΔH^*	-	enthalpy of activation for kinematic viscosity, cal/gm-mole
h	-	Planck's constant, erg/sec

J - diffusion flux, gm-moles/sec cm^2

k - Boltzmann's constant, erg/°K

L - length, cm

L_1 - length of non-radioactive capillary in shear-cell system, cm

L_2 - length of radioactive capillary in shear-cell system, cm

M_A - molecular weight of A, gm/gm-mole

M_B - molecular weight of B, gm/gm-mole

N_A - mole fraction of A

N_B - mole fraction of B

N_i - number of radioactive counts

N_o - Avogadro's number $(gm\text{-}mole)^{-1}$

R - gas constant, 1.98717 cal/gm-mole °K

ΔS^* - entropy of activation for kinematic viscosity, cal/gm-mole °K

t - time, sec

T - temperature, °K

V - molar volume, cm^3/gm-mole

Greek Symbols

β - experimentally determined concentration ratio in modified shear-cell technique

$\Delta\beta$ - error in β due to random nature of radioactive counting

γ - a configurational parameter dependent only upon the coordination number of the liquid

θ - parameter containing D in solution to Fick's second law for capillary-reservoir and shear-cell technique

λ_n - constant arising from solution to Fick's second law

ν - kinematic viscosity, cm^2/sec

ψ - experimentally determined concentration ratio in capillary-reservoir technique

Nomenclature for Computer Program

"Calculation of Self-Diffusion Coefficients"

DB - $\Delta\beta$

NRUN - RUN NUMBER

T - TIME OF RUN, SEC

SL1 - L_1, CM

SL2 - L_2, CM

CO - C_0, CPM

CS - C_S, CPM

C2T - $C_2(T)$, CPM

TEMP - T, °K

APPENDIX B

MATHEMATICAL ANALYSIS OF MODIFIED SHEAR-CELL DIFFUSION

The mathematical analysis for diffusion in the finite-capillary geometry of the modified shear-cell is given by Walls (1). Three assumptions are made: 1) the diffusion flux is described by Fick's first law, 2) the diffusion coefficient is independent of concentration, and 3) the volume change on mixing is zero.

Fick's second law is solved by separating the variables and using the following boundary and initial conditions:

$$\frac{\partial C(-L_1,t)}{\partial X} = 0 \qquad \text{(B-1)}$$

$$\frac{\partial C(L_2,t)}{\partial X} = 0 \qquad \text{(B-2)}$$

$$C(X,0) = C_S \qquad -L < X < 0 \qquad \text{(B-3)}$$

$$C(X,0) = C_0 \qquad 0 < X < L_2 \qquad \text{(B-4)}$$

$$C(X,\infty) = C_{avg} \qquad \text{(B-5)}$$

where:

C = concentration, cpm

L_1 = non-radioactive capillary length, cm

L_2 = radioactive capillary length, cm

t = time, sec

C_S = initial concentration on the non-radioactive side, cpm

C_0= initial concentration on the radioactive side, cpm

C_{avg}= average of C_S and C_0 at t =∞, cpm

X = capillaries, cm.

The general solutions is:

$$C(X,t) = A_o + \sum_{n=1}^{\infty} A_n e^{-(\lambda^2 Dt)} \cos \lambda_n (X-L_2) \qquad \text{(B-6)}$$

where:

$$\lambda_n = \frac{n\pi}{L_1 + L_2} \qquad \text{(B-7)}$$

$$A_o = \frac{1}{L_1 + L_2} \int_{-L_1}^{L_2} C(X,0)dX \qquad \text{(B-8)}$$

$$A_n = \frac{2}{L_1 + L_2} \int_{-L_1}^{L_2} C(X,0) \cos \lambda_n (X-L_2)dX \qquad \text{(B-9)}$$

By substituting Equation B-3 and B-4 into Equation B-8, the following is obtained:

$$A_o = \frac{C_S L_1 + C_0 L_2}{L_1 + L_2} \qquad \text{(B-10)}$$

Using the conditions of orthogonality, Equation B-9 is integrated to give:

$$A_n = (C_0-C_S) \left(\frac{2}{L_1+L_2}\right) \left(\frac{1}{\lambda_n}\right) \sin \lambda_n L_2 \qquad \text{(B-11)}$$

Integrating the general solution over the length of the radioactive capillary in Equation B-6 and dividing by L_2 yields:

$$C_2(t) = \frac{1}{L_2} \int_{0}^{L_2} C(X,t)dX \qquad \text{(B-12)}$$

The average concentration in the radioactive capillary when expressed as a function of time is:

$$C_2(t) = A_o + \frac{1}{L_2} \sum_{n=1}^{\infty} \frac{1}{\lambda_n} A_n e^{-\lambda n^2 Dt} \sin(\lambda_n L_2) \qquad \text{(B-13)}$$

Inserting the values for A_o and A_n into Equation B-13 gives:

$$C_2(t) = \frac{C_S L_1 + C_0 L_2}{L_1 + L_2} + \frac{2(C_0-C_S)(L_1+L_2)}{L_2 \pi^2} \sum_{n=1}^{\infty} \left[\frac{1}{n} \sin \frac{n \pi L_2}{L_1+L_2}\right]^2 x \left[\exp - \left[\frac{n \pi^2}{L_1+L_2}\right] Dt\right] \qquad \text{(B-14)}$$

Using the definitions:

$$\beta = 2\left[\frac{C_2(t)(L_1+L_2) - C_S L_1 - C_0 L_2}{(C_0 - C_S)(L_1 + L_2)}\right] \qquad \text{(B-15)}$$

and:

$$\theta = \frac{Dt}{(L_1 + L_2)^2} \qquad \text{(B-16)}$$

Equation B-14 becomes:

$$\beta = \frac{4(L_1 + L_2)}{\pi^2 L_2} \sum_{n=1}^{\infty} \left[\frac{1}{n} \sin\left(\frac{n \pi L_2}{L_1+L_2}\right)\right]^2 \exp - (n\pi)^2\theta \qquad \text{(B-17)}$$

Equation (B-17) is the solution to Fick's second law and for the modified shear-cell.

The value, β, is the experimentally determined concentration ratio. The random error in β can be calculated in terms of the individual random counting error associated with each radioactivity measurement as:

$$\Delta\beta = \frac{2}{C_0-C_S}\left[(\Delta C_2(t))^2 + \left[\frac{C_2(t)-C_2}{C_0-C_S}\right](\Delta C_0)^2 + \left[\frac{C_0-C_2(t)}{C_0-C_2}\right]^2 (\Delta C_S)^2\right]^{1/2} \qquad \text{(B-18)}$$

where ΔC_i, the error in the individual count rate is expressed in terms of the total number of counts, N_i, as:

$$\Delta C_i = C_i (N_i)^{-1/2}$$

APPENDIX C

COMPUTER PROGRAM FOR CALCULATION OF DIFFUSION COEFFICIENTS AND INSTRUCTIONS FOR IT'S USE

The iterative scheme used to calculate θ and the self-diffusion coefficient in Equation B-17 involves calculating a θ_1 value from the first term approximation of the experimentally derived β value. This θ_1 value is then used to evaluate the series solution and the difference between the computed value $\bar{\beta}$ and β is given as:

$$H_i = \frac{4}{\pi^2}\frac{L_1+L_2}{L_2}\sum_{n=0}^{N}\left[\frac{1}{n}\sin\frac{n\pi L_2}{L_1+L_2}\right]^2 \exp[-(n\pi)^2\theta]-\beta = \bar{\beta} - \beta \qquad \text{(C-1)}$$

Using the Newton-Raphson method, θ_i is iterated to determine that value of θ_i which reduces H_i to some specified limit; i.e.:

$$\theta_{i+1} = \theta_i - H(\theta_i)/H'(\theta_i) \qquad \text{(C-2)}$$

in which the subscript i denotes the number of iterations. It was found that five iterations, N = 5 in equation C-1, gave sufficient accuracy for θ_i, and to calculate D, the value of H_i was less than .000000001.

The program used to calculate the diffusion coefficient is shown in Figure 3. For run number 34 the following data were collected:

DB = .0023 (calculated from Equation C-18)

NRUN = 34

T = 33175 sec

SL1 = 3.10 cm

SL2 = 3.01 cm

CO = 36494 cpm

C2T = 30120 cpm

CS = 20 cpm

TEMP = 375.7°K

The program, "Calculation of Self-Diffusion Coefficients", calculated these values:

NRUN	T	SL1	SL2	CO	CS	C2T	TEMP	1000/T
34	33175	3.10	3.01	36494	20.0	30120	375.7	2.662

D 10-5	BETA	D-BETA	THETA
2.779	.6358	.0023	.02470

The program must be run twice to calculate the change in the self-diffusion coefficient shown in Table 1. Positive and negative values of DB are read into the program and a card is inserted setting BETA equal to BETA plus DB.

```
C
C                    CALCULATION OF SELF-DIFFUSION COEFFICIENTS
C
      DIMENSION P(20)
      PI = 3.1415926
      WRITE(6,10)
    1 M = 0
      READ(5,20,END=5)DB,NRUN,T,SL1,SL2,CO,CS,C2T,TEMP
      RL = SL2/(SL1 + SL2)
      BET1 = C2T * (SL1 +SL2) -CS*SL1 - CO*SL2
      BET2 = ((CO - CS) * (SL1 + SL2))
      BETA = 2.0*(BET1/BET2)
      THETA = -(1/(PI**2))*ALOG((PI*PI*BETA*RL)/(4.*(SIN(PI*RL)**2)))
    2 HP = 0
      H  = 0
      DO 3 N = 1,5
      P(N) = ((SIN(N*PI*RL))**2)*EXP(-((N*PI)**2)*THETA)
      HP = HP + P(N)
    3 H  = H  + P(N)/(N*N*PI*PI)
      HP = -4.*HP/RL
      H  =  4.*H/RL - BETA
      THETA = THETA - H/HP
      M = M + 1
      IF(M.GT.10) GO TO 4
      HA = ABS(H)
      IF (HA.GT.0.000000001) GO TO 2
    4 CONTINUE
      D = 100000* (SL1 + SL2)**2/T*THETA
      TEM =  1000./TEMP
      WRITE(6,30)NRUN,T,SL1,SL2,CO,CS,C2T,TEMP,TEM,D,BETA,DB,THETA
      GO TO 1
    5 CONTINUE
      STOP
   10 FORMAT(1H1,3HRUN,5X,1HT,7X,3HSL1,4X,3HSL2,5X,2HCO,6X,2HCS,5X,3HC2T
     1,6X,4HTEMP,2X,6H1000/T,4X,6HD*10-5,4X,4HBETA,4X,6HD-BETA,4X,5HTHET
     2A/)
   20 FORMAT(F8.0,I2,7F10.0)
   30 FORMAT(1X,I4,F9.0,2F7.2,F9.0,F7.1,F9.0,F8.1,F8.3,3F9.4,F10.5)
      END
```

Figure 4. Computer Program, "Calculation of Self-Diffusion Coefficients"

APPENDIX D

SELF-DIFFUSION COEFFICIENTS FROM THE WALLS-UPTHEGROVE EQUATION

The Walls-Upthegrove equation has been given as:

$$D = \frac{k\ T\ \gamma^{-1/3}}{2\pi hb(2b+1)} \left(\frac{V}{N_o}\right)^{2/3} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \qquad (13)$$

Walls (24) has given the values of b and γ as .419 and 4/3 respectively. The values of ΔH^* and ΔS^* can be found by curve fitting the viscosity data of Foley, Basak, and Delorey to the following equation:

$$\nu = B \exp\left(\frac{\Delta H^*}{RT}\right) \qquad (19)$$

which results in:

$$\nu = .000427 \exp\left(\frac{610.92}{RT}\right)$$

ΔS^* is found by solving equation (20):

$$B = \frac{N_o\ h \exp\left(\frac{-\Delta S^*}{R}\right)}{N_{Tl}M_{Tl}+N_{Hg}M_{Hg}} \qquad (20)$$

Substituting values:

$$.000427 = \frac{(6.02\text{x}10^{23})(6.62\text{x}10^{-27}) \exp\left(\frac{-\Delta S^*}{1.987}\right)}{(.014137)(204.39)+(.98586)(200.61)}$$

and:

$$\Delta S^* = -1.54406$$

The self-diffusion coefficient will be evaluated at 298.2°K. The only unknown value left to be found is the molar volume of the amalgam at 298.2°K. The molar volume for 1.440 weight % amalgam is found

from the density data of Foley, Basak, and Delorey (44) to be 14.863 cm^3/mole. Substituting the values into equation (13) gives:

$$D = \left[\frac{(1.38\times10^{-16})(298.2)(4/3)^{-1/3}}{2(3.14)(6.62\times10^{-27})(.419)(.419+1)}\right]\left(\frac{14.863}{6.02\times10^{23}}\right)^{2/3}\exp\left(\frac{-1.544}{1.987}\right)\times$$

$$\exp\left(\frac{-610.92}{(1.987)(298.2)}\right) = 1.64 \times 10^{-5}\ cm^2/sec$$

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